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Interaction of Remote Functional Groups (Amide and Amine) in Steroidal Compounds After Electron Ionization

Pierre Longevialle†
ICSN–CNRS, 91190 Gif sur Yvette, France

Guy Bouchoux and Yannik Hoppilliard
DCMR, Ecole Polytechnique, 91128 Palaiseau Cedex, France

Electron impact ionization of steroidal compounds with two differently substituted functional groups (amide and amine) at remote positions leads to the interaction of these groups in ion–neutral complexes after the detachment of one of them. Two situations may be encountered, depending on which group is more easily detached from low-energy parent ions: (i) when the formation of the immonium ion is preferred, a very efficient proton transfer to the amide is observed leading to abundant [M – imine]$^{+\cdot}$ and subsequent daughter ions; (ii) when the detachment of the amide is preferred, hydrogen exchanges occur with the amine group, and fragment ions may be observed resulting from the addition of both groups in a proton-bound structure.

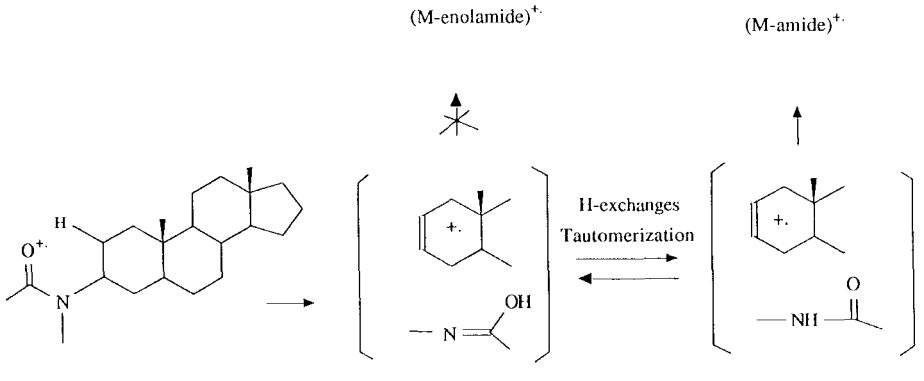
INTRODUCTION

Bifunctional steroids have provided, under electron impact, many examples of reactions between functions at remote sites of the parent ion.[1,2] These reactions are particularly illustrative of the intermediacy of complexes[3–5] in which large and rigid fragments (ions and neutral species) remain associated after their detachment and are mutually oriented under the influence of ion–dipole interactions. By this process, polar groups originally separated by large distances may be brought together and undergo reactions which would not otherwise be possible in the intact parent ion.

In a previous paper, intermediate ion–neutral complexes were shown to play an important role in the unimolecular fragmentation of steroidal amides under electron ionization (EI).[6] In the case of 3-*N*-methylacetamido steroids, the initial detachment of the functional group from C(3) after a McLafferty-type H transfer leads to [M – *N*-methylacetamide]$^{+\cdot}$ and [protonated *N*-methylacetamide]$^{+\cdot}$ ions which are dominant at low (mass-analysed ion kinetic energy spectrum, MIKES) and high (70 eV) energy, respectively. It was shown by thermochemical arguments that the loss of *N*-methylacetamide is accompanied by enolamide-to-amide tautomerization within the ion–neutral complexes. This process involves H exchanges, explaining also the observed lack of site specificity in the origin of the H transferred (Scheme 1).

In this context, an additional polar group has been introduced in 3-amido steroids (Scheme 2) at a remote position from C(3), in order to examine what kind of interaction it may undergo in the complex with the neutral amide (or enolamide) detached from C(3), expecting that this new function would behave as a preferential site of reactivity.[7]

† Author to whom correspondence should be addressed.



Scheme 1

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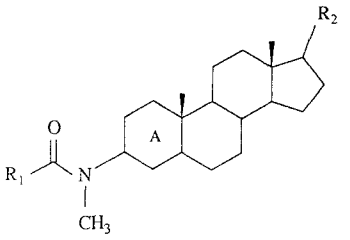


	R_1	R_2
1	CH_3	$-CH(CH_3)-NH_2$
2	CH_3	$-CH_2-NH-CH_3$
3	H	$-CH_2-NH_2$
4	CH_3	$-CH_2-NH_2$
5	C_2H_5	$-CH_2-NH_2$

Scheme 2

RESULTS AND DISCUSSION

The introduction of a new function in a 3-amido steroid, for the above purpose, leads to a delicate problem: the detachment of the amide from C(3) must remain the preferred decomposition process of the parent ions of low internal energy, i.e. the other functional group must not induce any decomposition process of lower critical energy than the amide detachment. Otherwise, the loss of amide might not be observed at all, or may suffer a competition such that the neutral amide fragment would be produced with too much translational energy in the reaction coordinate and rapidly separate from the $[M - amide]^{+\cdot}$ ion without reacting in a complex. The additional functional group should, nevertheless, localize the charge *after* the detachment of the neutral acetamide from C(3) and become the preferential site of reactivity of the ion.

In this regard, compounds **1**–**5** (Scheme 2) represent an array of different situations reflected in their *MIKE* spectra (Table 1) and conventional EI mass spectra (Figs. 1–5).

Table 1. MIKE spectra of compounds 1–5 (relative abundances)

Compound	$[M - imine]^{+\cdot}$	$[M - amide]^{+\cdot}$
1	100 (*m/z* 331)	—
2	100 (*m/z* 331)	—
3	100 (*m/z* 317)	60 (*m/z* 287)
4	10 (*m/z* 331)	100 (*m/z* 287)
5	8 (*m/z* 345)	100 (*m/z* 287)

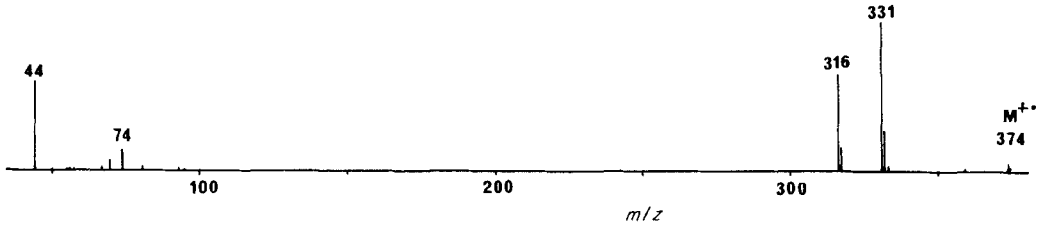


Figure 1. 70-eV EI mass spectrum of **1**.

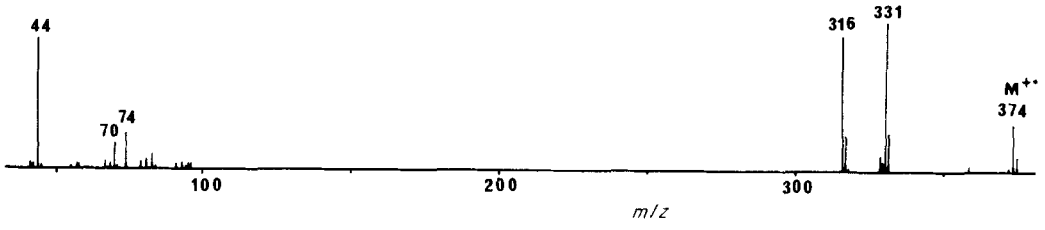


Figure 2. 70-eV EI mass spectrum of **2**.

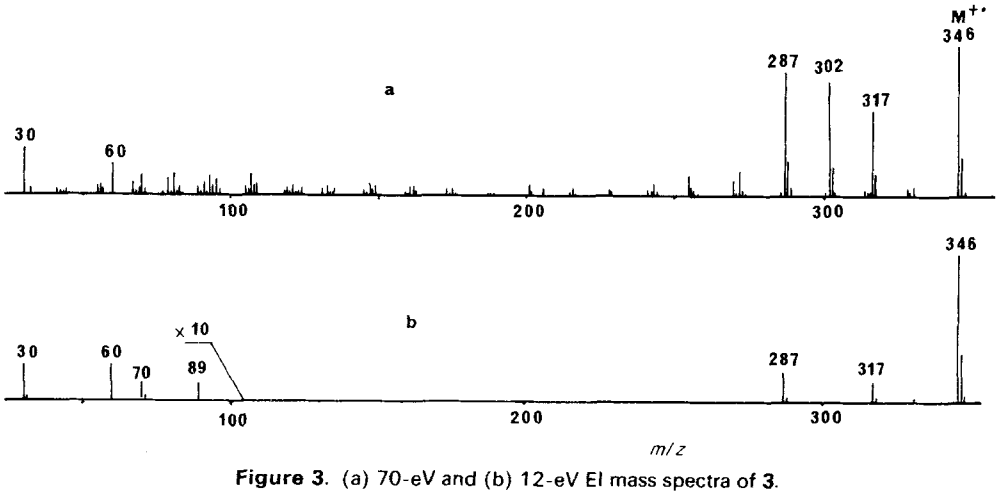


Figure 3. (a) 70-eV and (b) 12-eV EI mass spectra of **3**.

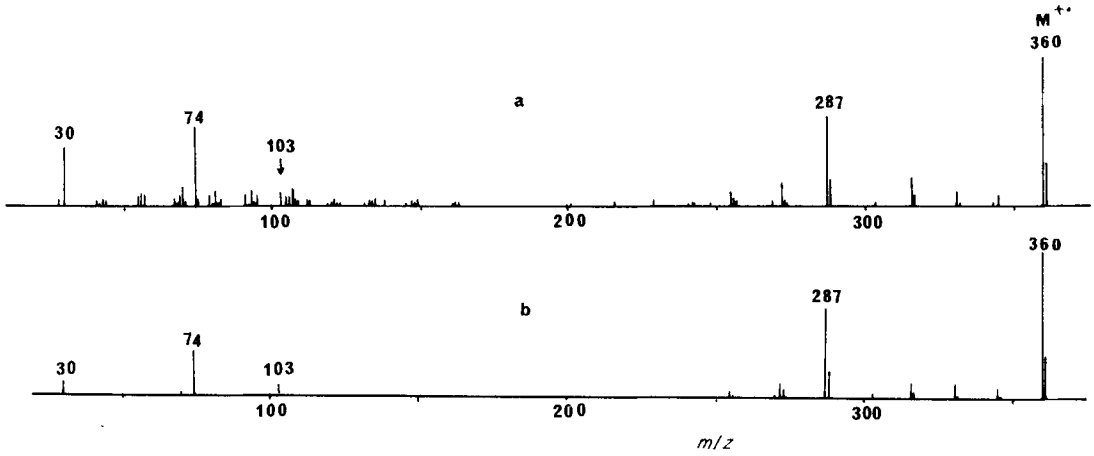


Figure 4. (a) 70-eV and (b) 12-eV EI mass spectra of **4**.

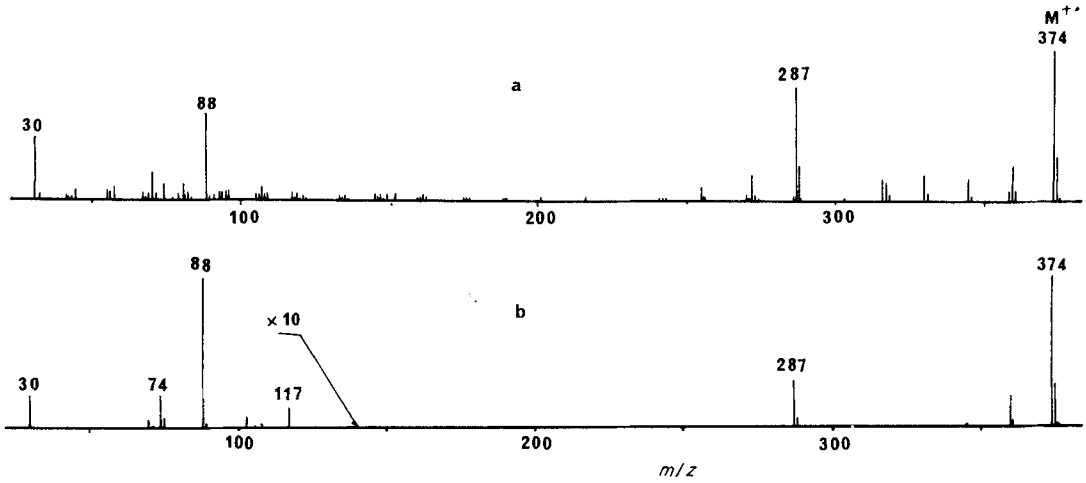


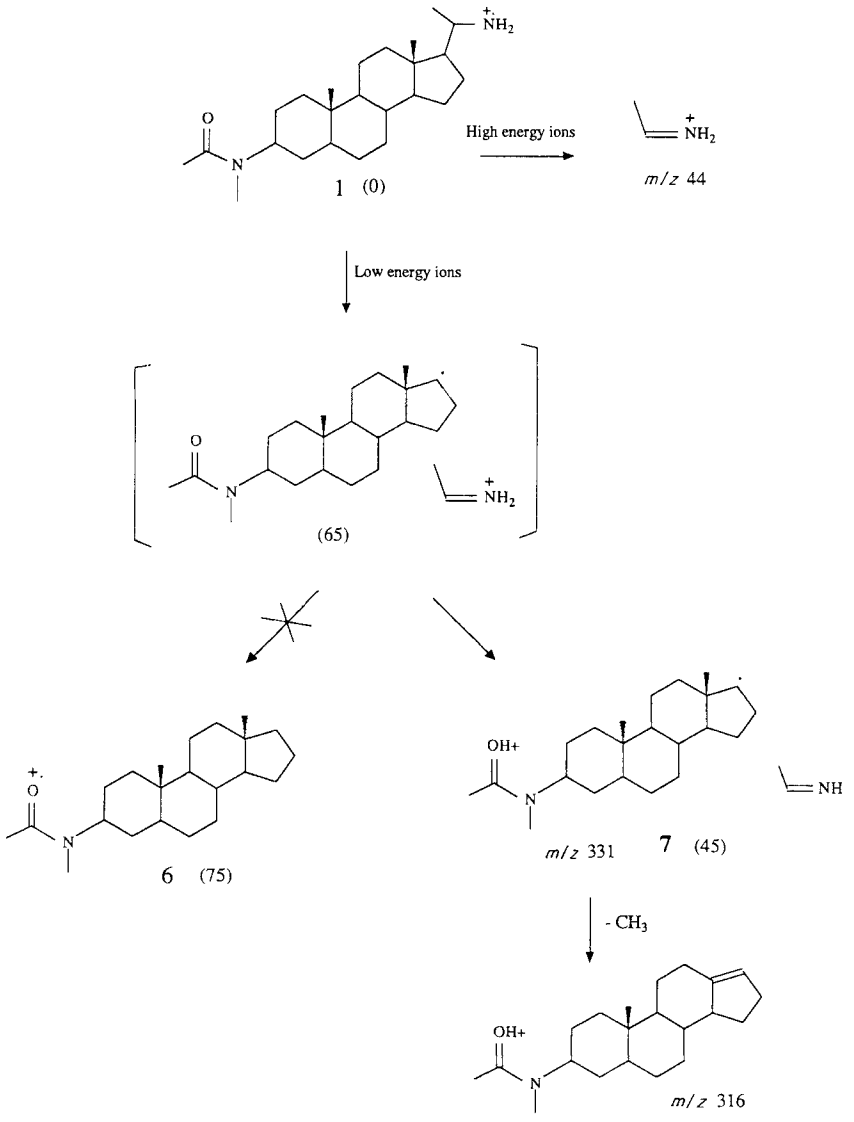
Figure 5. (a) 70-eV and (b) 14-eV EI mass spectra of **5**.

For **1** and **2** the fragmentations induced by the amine function are dominant. A single Gaussian-shaped peak is observed in the MIKE spectrum of **1** for [M − acetaldimine]$^{+\cdot}$ ions at *m/z* 331 (Scheme 3). This is also the major signal in the 70-eV mass spectrum in addition to peaks at *m/z* 44, [protonated acetaldimine]$^+$, and *m/z* 316, [M − acetaldimine − methyl]$^+$. The loss of amide is not detected and only a small peak at *m/z* 74, [amide + H]$^+$, is present. The preferred decomposition pathway of ions of *m/z* 331 from **1** and **2** (MIKES) is the loss of a methyl radical. This process is of minor importance for the isomeric 3-methylacetamidoandrostane **6** decomposing mainly into [**6** − amide]$^{+\cdot}$ and [amide + H]$^+$ ions.[6] Clearly, the substantial loss of acetaldimine from **1** is a new example of the reaction reported before:[1,2] after its detachment from C(17), the immonium ion protonates, in an ion–neutral complex, the most basic site of its neutral partner. The known thermochemical data† reveal that the oxygen of the amide function at C(3) is more basic than the radical at C(17) by ~30 kJ mol^{-1}. Further, the distonic ion **7** has a labile methyl group at the α-position to the radical site. Therefore, the formation of **7** rather than **6** (Scheme 3) in this reaction is readily explained by thermochemical and structural arguments.

The heat of formation of the final state, consisting of the fragment ion of *m/z* 44 and the accompanying neutral fragment, is larger than that of **7** + $CH_3CH{=}NH$ by ~20 kJ mol^{-1} (difference between proton affinities of acetaldimine and *N*-dimethylacetamide[8]), in agreement with the presence of only a peak at *m/z* 331 in the MIKE spectrum of **1**. The same argument holds for **2**.

In the case of **3** the fragmentation of the amine is more difficult, and the 70-eV EI mass spectrum (Fig. 3) shows clearly the competition between the reactivity of the amine: *m/z* 30, [protonated formaldimine]$^+$; *m/z* 317, [M − formaldimine]$^{+\cdot}$; *m/z* 302, [M − formaldimine − methyl]$^+$; and the reactivity of the amide: *m/z* 287, [M − amide]$^{+\cdot}$; and *m/z* 60, [protonated amide]$^{+\cdot}$. At low ionizing energy (12 eV, Fig. 3(b)) the situation is comparable except that the secondary ion of *m/z* 302, [M − formaldimine − methyl]$^{+\cdot}$, is absent and an interesting signal corresponding formally to an [amide + protonated

† The thermochemistry associated with Scheme 3 was estimated from ionization energy *IE*(**1**) = *IE*(*sec*-butylamine) = 820 kJ mol^{-1}, *IE*(**6**) = *IE*(*N*,*N*-dimethylacetamide) = 850 kJ mol^{-1}, *IE*(H$^{\cdot}$) = 1312 kJ mol^{-1}, proton affinity *PA*($CH_3CH{=}NH$) = 890 kJ mol^{-1}, $\Delta H_f^\circ[CH_3CH{=}NH]^+$ = 657 kJ mol^{-1}, *PA*(*N*,*N*-dimethylacetamide) = 910 kJ mol^{-1}, *BDE*(secondary C—H bond) = 415 kJ mol^{-1} and $\Delta H_f^\circ(H^{\cdot})$ = 218 kJ mol^{-1}. All these data originate from Ref. 8. The heats of formation of the neutral species were estimated with the Benson's increment method.[9]



Scheme 3. Values in kJ mol^{-1}.

formaldimine]$^+$ ion appears at *m/z* 89 (see later). The MIKE spectrum of **3** exhibits two major peaks at *m/z* 317 (100%) and *m/z* 287 (60%).

In the cases of **4** ($R_1 = CH_3$) and **5** ($R_1 = C_2H_5$), the fragmentation induced by the amide group is favoured (Figs 4 and 5): the signals of [M − amide]$^{+\cdot}$ at *m/z* 287 and [amide + H]$^+$ at *m/z* 74 and 88, respectively, dominate over those of the [protonated formaldimine]$^+$ at *m/z* 30 and of [M − formaldimine]$^{+\cdot}$. The latter peaks decrease on lowering the ionizing energy (Figs 4(b) and 5(b)) or when sampling metastable parent ions **4** and **5** (Table 1). All these observations agree with the formation of ions of low heats of formation such as those shown in Scheme 4.

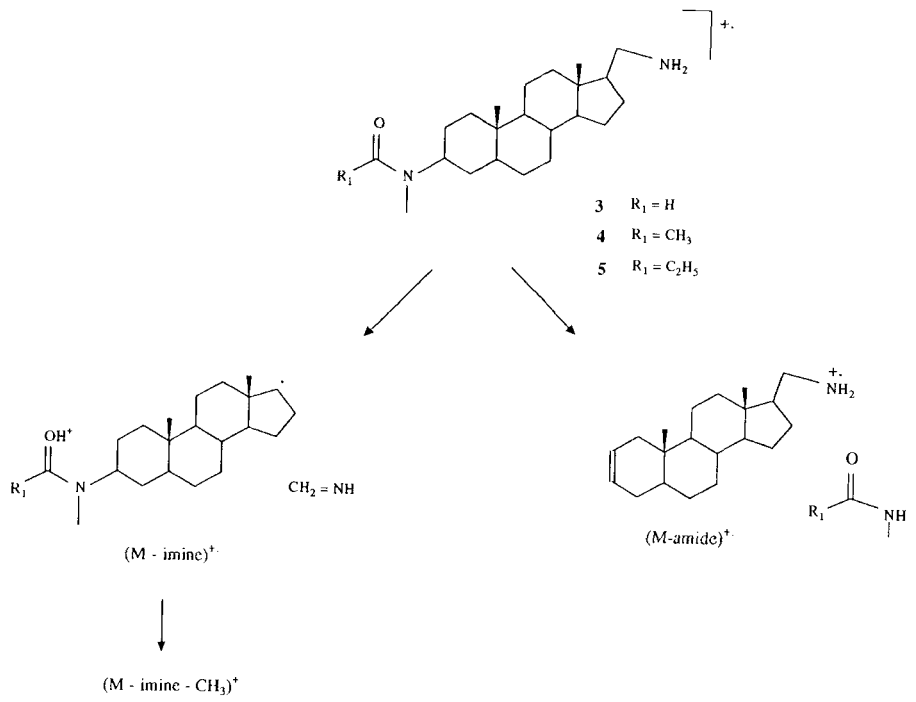
Ions *a*

The presence of peaks at *m/z* 103 and 117 in the 12-eV mass spectra of **4** and **5**, respectively, is particularly interesting. These ions, mentioned above in the case of **3** (*m/z* 89), will be denoted hereafter ions *a*. Their *m/z* ratio corresponds to an adduct [amide + formaldimine + H]$^+$ and, in this case, they should arise from a reaction between both functional groups initially distant in the parent ion. This phenomenon is of particular importance with respect to the concept of ion–neutral complexes and will be discussed in more detail.

First it should be emphasized that the set of examples studied, **1**–**5**, clearly shows that the ions *a* only appear if the initial detachment of the amide from C(3) is dominant at low energy. This strongly indicates that ions *a* originate from the interaction of the detached amide with the amine group and not from the interaction of the detached imine or immonium ion with the amide function at C(3).

After the detachment of the amide moiety from C(3) the charge would be preferentially localized at the amine function of the steroid. Therefore, the formation of ions *a* is apparently the result of an ion–neutral reaction between the amide moiety and the ionized amine group.

The structure of ions *a* may be inferred from its subsequent characteristic decompositions. The MIKE spec-

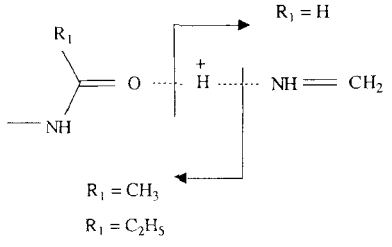


Scheme 4

trum of *a* shows peaks at *m/z* 30 in the case of **3** and at *m/z* 74 and 88 in the cases of **4** and **5**, respectively. These results match perfectly with the relative proton affinities of formaldimine (865 kJ mol^{-1})[10] on the one hand and of *N*-methylformamide (861 kJ mol^{-1}),[8] *N*-methylacetamide (888 kJ mol^{-1}, estimated) and *N*-methylpropylamide (895 kJ mol^{-1}, estimated) on the other. Further, the corresponding kinetic energy releases are small: $T_{0.5}$ = 9, 11 and 14 meV for **3**, **4** and **5**, respectively.

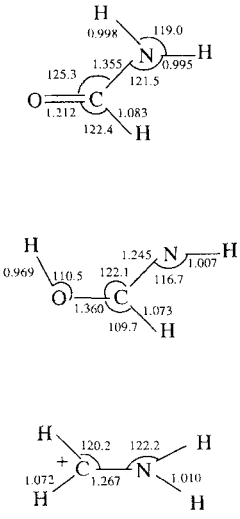
These two sets of information suggest that the dissociating configuration of ions *a* resembles its separated products, i.e. formaldimine and *N*-methylacetamide, $R_1CONHCH_3$ (not the amide enol tautomers which are ~60 kJ mol^{-1} less stable[6]). The most obvious structure for reactive ions *a* is thus a proton-bound structure a_1 (Scheme 5).

Ion *a* (a_1)

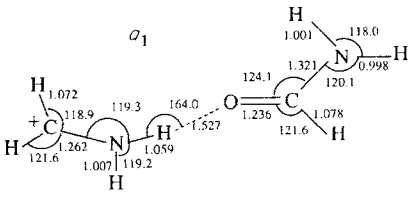


Scheme 5

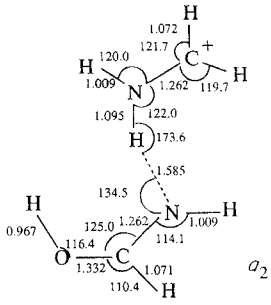
Other possibilities may exist, however. In order to study these alternatives, several proton-bound associates involving the simplest species $HCONH_2$ and $[CH_2{=}NH_2]^+$ were investigated by *ab initio* molecular orbital calculations. It has been shown that reasonably



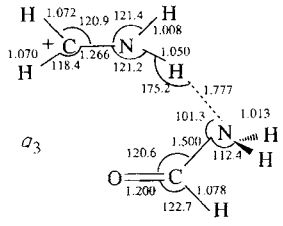
good relative energies of amide/enolamide tautomers are given by *ab initio* calculations at the 3-21G//3-21G level.[6] The introduction of a polarized basis set and of an electron correlation effect (MP2/6-31G*//3-21G) reduces only slightly (by 10%) the energy difference between amide and enolamide. Consequently, the system $HCONH_2/[CH_2{=}NH_2]^+$ was investigated with full geometry optimization with the 3-21G basis set of atomic orbitals. Total and relative energies evaluated at this level are given in Table 2. It appears that at least four structures involving either formamide or its enol interacting with $[CH_2{=}NH_2]^+$ have binding energies between 20 and 150 kJ mol^{-1}. Structure a_1 is the most stable adduct. However, the proton affinities render structures a_3, for R_1 = H, and structures a_2, for $R_1 = CH_3$ or C_2H_5, also possible. Moreover, the structures of the hydrogen-bonded species *a* differ according to R_1. For a_1 and a_2 the proton is covalently bonded to



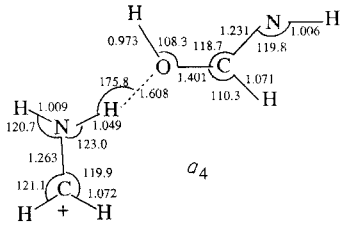
a_1



a_2



a_3



a_4

the nitrogen atom of the formaldimine when $R_1 = H$; the situation is reversed when $R_1 = CH_3$ or C_2H_5, as indicated by partial geometry optimization (3–21G basis set). As expected and known from other cases,[11] the proton is always covalently bonded to the most basic moiety.

Whether the amide moiety has the enol or keto structure when transferred from C(3) to the amine function

Table 2.

Compound or ion	E (321G//3–21G) (hartree)	ΔE (kJ mol^{-1})
$HCONH_2 + CH_2NH_2$	−261.84774	0
$HOCH{=}NH + [CH_2NH_2]^+$	−261.81967	+74
a_1	−261.90466	−149
a_2	−261.86232	−38
a_3	−261.84847	−54
a_4	−261.85504	−19

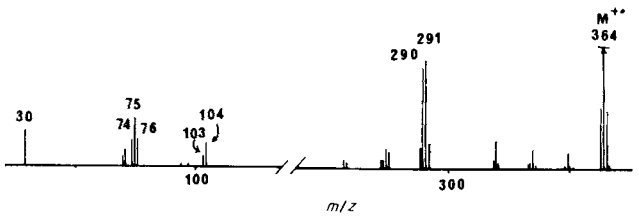
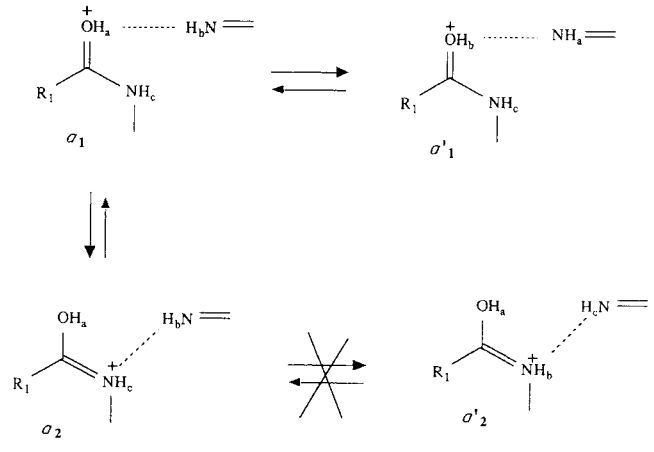


Figure 6. 18-eV EI mass spectrum of **4**-d_4.

at C(20) was investigated by deuterium-labelling experiments. The tetradeuterated derivative **4**-d_4-C(2)C(4) (Fig. 6) generates the $[M - amide]^{+\cdot}$ ion as a mixture of d_0 (m/z 290) and d_1 (m/z 291) ions, as described previously,[6] and the [protonated amide]$^+$ ions as a mixture of d_0 (m/z 74), d_1 (m/z 75) and d_2 (m/z 76) ions. The reason for this lack of regioselectivity is H–D exchanges in the intermediate ion–neutral complexes before decomposition.[6] In this case, ions a correspond to a mixture of d_0 (m/z 103) and d_1 (m/z 104) ions in an abundance ratio of about 1:2, respectively (Fig. 6). It may be noted that the absence of any (d_2) ion a (m/z 105) rules out the possibility of a reaction of the protonated amide detached from C(3) with the amine at C(20). Two other D-labelled derivatives with one and two D atoms at the amine function (denoted **4**-d_1 and **4**-d_2, respectively) were also examined. Figure 7 shows the MIKE spectra of the m/z 104 ion from **4**-d_4 (case 1), m/z 105 ion from **4**-d_2 (case 2) and m/z 104 ion from **4**-d_1 (case 3).

In cases 1 and 2 the peak-height ratios approach 1:1, indicating the exchange of two atoms, H and D. The slight predominance of the peak at m/z 75 cannot be due to a small contribution of an exchange between three atoms since this would lead to a larger m/z 76 peak in case 2, contrary to observation. In case 3 the ratio of the peak heights m/z 75/74 is 2.5, i.e. fairly close to 3. This may be interpreted again by the exchange between two atoms (H and D) operating only for half of the population of the m/z 104 precursor ions.

These results lead to the conclusion that one H (or D) of the amine group is irreversibly transferred to the amide (or enolamide) moiety and that the H–D exchanges involve the two other atoms: the H at the imine nitrogen and the mobile H (or D) of the amide (or enolamide) group. A possible mechanism is presented in Scheme 6 for the most stable structures a_1 and a_2 (the



Scheme 6

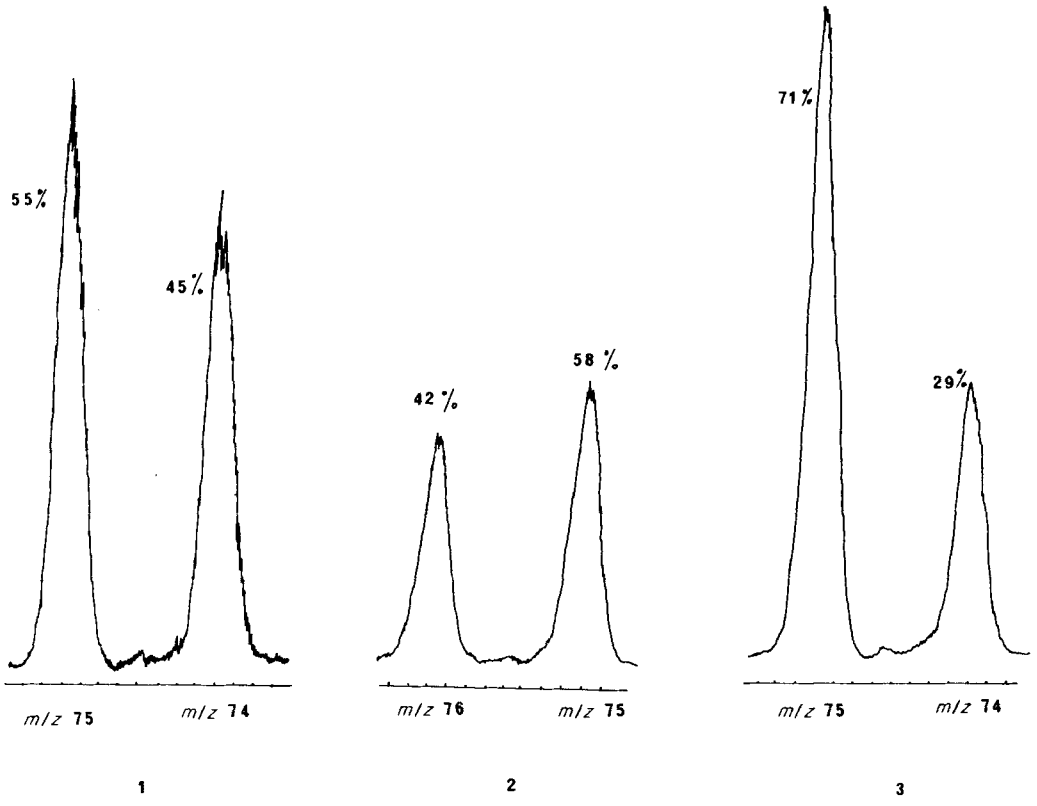


Figure 7. MIKE spectra of (1) ions m/z 104 from **4**-d_4; (2) ions m/z 105 from **4**-d_2; (3) ions m/z 104 from **4**-d_1.

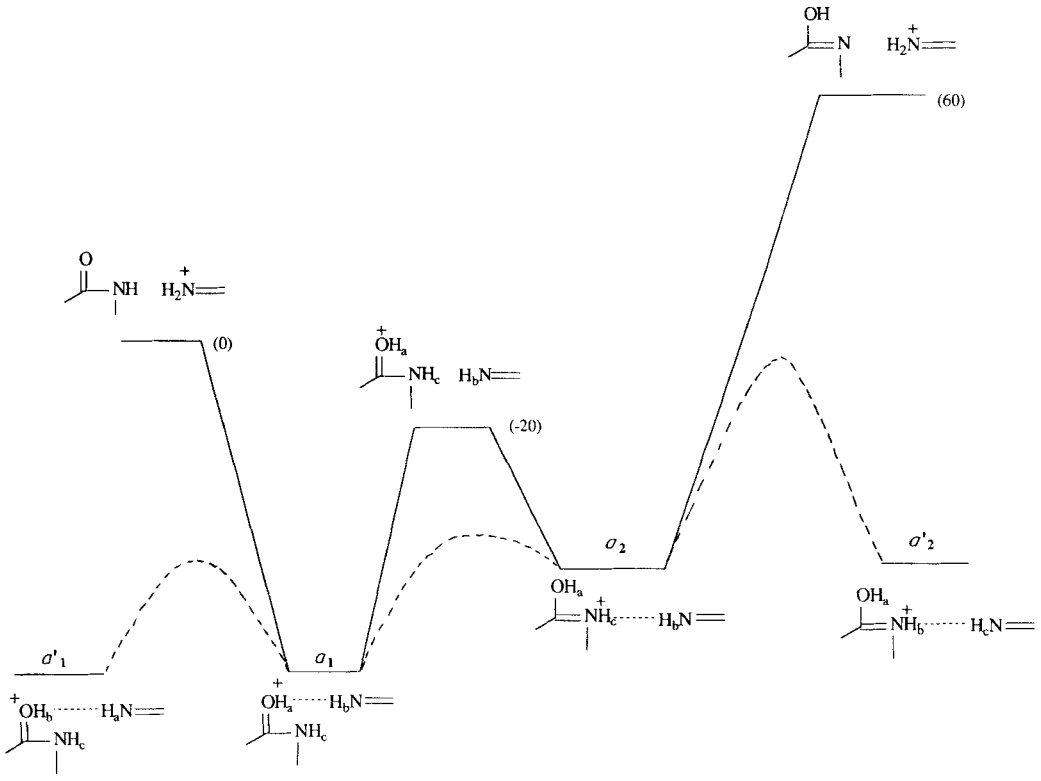


Figure 8. Schematic energy profile for the reactions of ion a (kJ mol^{-1}).

proton is shown covalently bound to the amide, as expected for $R_1 = CH_3$ or C_2H_5).

Clearly, the occurrence of all the processes $a_1 \rightleftharpoons a_2$, $a'_1 \rightleftharpoons a'_2$, $a_1 \rightleftharpoons a'_1$ and $a_2 \rightleftharpoons a'_2$ would equilibrate all three atoms H_a, H_b and H_c. The fact that it is not observed shows that one step in Scheme 6 is not allowed. A qualitative view of the energy profile associated with Scheme 6 is presented in Fig 8.† The upper limit of the transition state energy for an internal reorientation within loose associations is given by the energy of the separated partners. Obviously $a_1 \rightleftharpoons a_2$ is an easy process, and it seems reasonable to assume that $a_1 \rightleftharpoons a'_1$ is easier than $a_2 \rightleftharpoons a'_2$ since the completed proton transfer on the formaldimine requires 150 kJ mol^{-1} from a_2 but only 110 kJ mol^{-1} from a_1 (Fig. 8). Consequently, and in order to account for the experimental results, it is proposed that the forbidden exchange reaction is the $a_2 \rightleftharpoons a'_2$ process. Since this proposal requires that the amine H atom (H_c) is irreversibly attached to the amide, it follows that it is the enolamide (and not the amide) which interacts with the amine function in the formation of ions *a*.

It is also noteworthy that ions *a* are absent from the MIKE spectra. Their signal appears in the 70-eV EI mass spectra and is enhanced at lower ionization energy (12 eV). This indicates that they are not formed from metastable parent ions but rather from the least energized parent ions among those decomposing in the ion source.

CONCLUSION

From the experimental results, the decomposition of compounds **1–5** under EI ionization may now be formulated as follows.

In the case of **1** and **2**, the usual fragmentation of the amine function is very dominant. The loss of an alkylimine is particularly important, resulting from a proton transfer from the detached immonium ion to the amide group in an ion–neutral complex.[1]

In contrast, in the case of **4** and **5**, the loss of an amide is the most favoured decomposition pathway and the case of **3** is intermediate. It has been shown previously[6] that 3-*N*-methylacetamido steroids fragment preferentially by the loss of *N*-methylacetamide from C(3). This occurs by a McLafferty-type H transfer from C(2) or C(4) to the carbonyl group followed by the C(3)—N bond rupture and detachment of the enolamide (Scheme 1). The loss of the enolamide is a high energy demanding process and does not occur. Instead, H exchanges take place in the ion–neutral complexes resulting in the tautomerization of the enolamide into an amide, which is more easily lost. Most of the parent ions **4** and **5** also decompose by the same process and lose the amide from C(3) after tautomerization. The presence of ions *m/z* 76 containing two D atoms and *m/z* 103 with no D atom, however, in the 18-eV EI mass spectrum of **4**-d_4 shows that, for a certain fraction of the parent ions, the enolamide detached from C(3) reacts further, either by picking up a second D atom from ring A leading to *m/z* 76 ions, or by exchanging its original D atom with H, leading to ions *a* of *m/z* 103, with the amide component probably in a 'keto' structure.

However, a new process appears (Scheme 7): for a fraction of the parent ions which are slightly more energized than metastable ions, the amide moiety detached from C(3) does not separate from the parent ion but, instead, is reoriented in the ion–neutral complex and approaches the amine function at C(20) carrying the positive charge.

The exothermic transfer of a proton from an ion to a neutral molecule is a most favourable reaction. Here, two mobile H atoms are present at the ionized amine function and one of them is used for a hydrogen bond to the amide group, creating more radical character at the amine group. The proton transfer may go to completion, leading to the protonated amide, which may either separate from the complex or return a proton back to the amine and depart as a neutral amide. In competition with this process, the *C(17)—C(20) bond* rupture, which has become more facile because of the proton bonding in the fragment ion, may occur, leading to the proton-bound ions *a* decomposing further according to the proton affinities of the partners.

The extent of H–D exchanges in D-labelled derivatives shows that most of the amide moieties escaping from ring A and reacting with the amine have conserved the enolamide structure. A small fraction of amides transferred with the 'keto' structure, however, may be responsible for the slight excess observed (Fig. 7) in the abundance of ions *m/z* 75 compared with what it should be in the case of 100% enolamide.

In the model proposed, the amide tautomerization occurs prior to further H exchanges. The ions *a* are observed in the mass spectra simply because the C(17)—C(20) bond rupture competes with the 'normal' H-exchange process between the amine and the amide moiety.

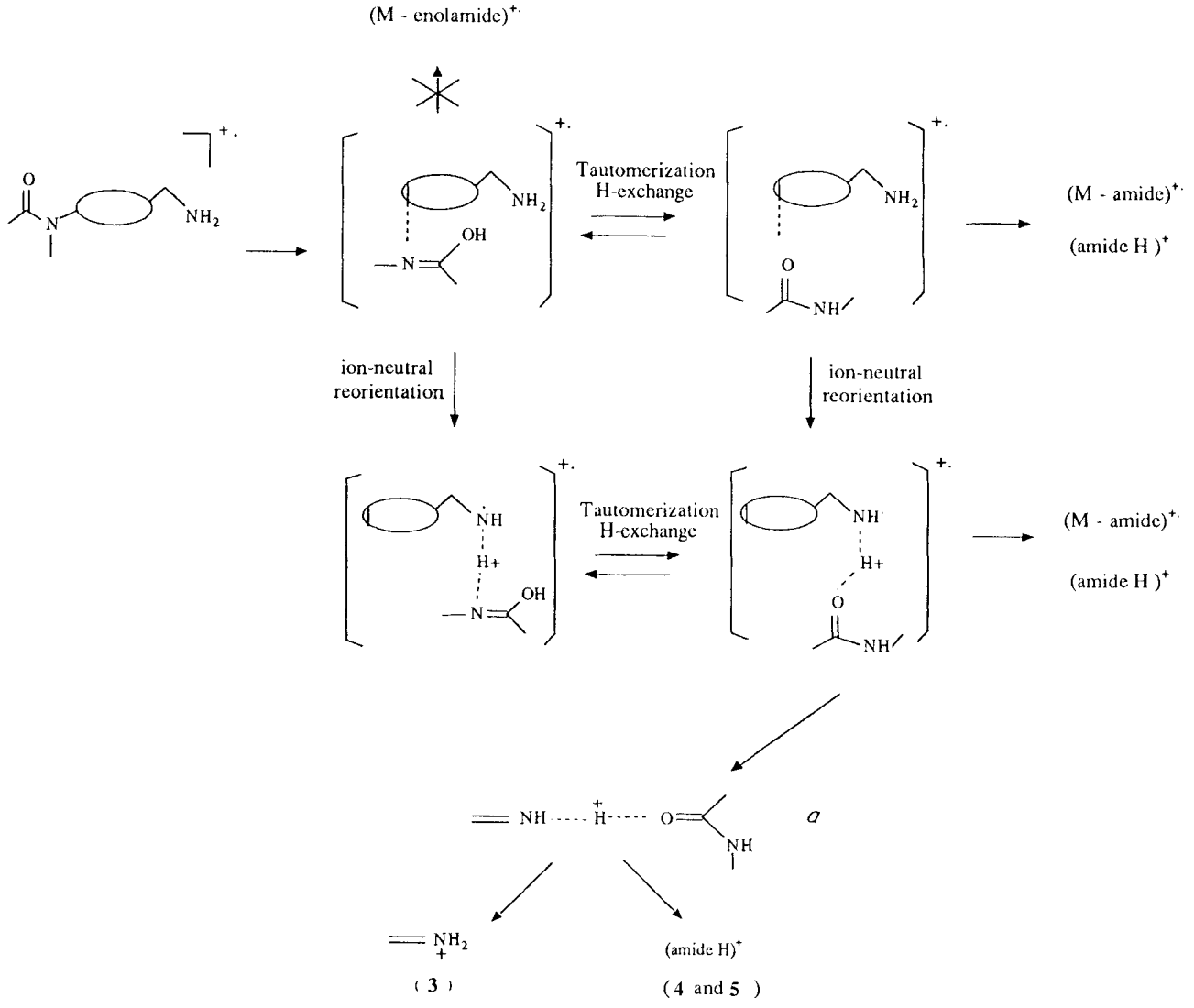
The formation of ions *a* described here strongly confirms the intermediacy of ion–neutral complexes in the unimolecular fragmentation of organic compounds. It shows, moreover, that reactions between ion and neutral in complexes are not limited to proton transfers, as most generally reported, but occasionally may be more complex. In the present examples, an internal addition of groups of atoms detached from remote sites of the parent ion is observed (a comparable reaction has been reported in the fragmentation under EI of trimethylsilyl derivatives of sterols[12]).

The formation of ions *a* also appears exceptional because it is not the reaction of lowest critical energy of the parent ion (metastable parent ions do not lead to ions *a*) although involving an ion–neutral complex.

EXPERIMENTAL

The EI mass spectra were measured with an MS 50 instrument and MIKE spectra with a ZAB 2F instru-

† Heats of formation of the various covalent species presented in Fig. 8 were taken equal to a -236,[8] 406,[6] -179,[6] 745[10] and 80[11] kJ mol^{-1} for $CH_3CONHCH_3$, $[CH_3C(OH)NHCH_3]^+$, $CH_3C(OH)NCH_3$,[6] $[CH_2NH_2]^+$ [10] and $[CH_2NH]^+$,[11] respectively. Binding energies of the complexes were crudely estimated by considering the results of MO calculations quoted in Table 3.



Scheme 7. The steroid skeleton is symbolized by an ellipse.

ment. The samples were vaporized into the ion source by direct introduction at the minimum temperature for volatilization (150–200 °C). The trap current was 100 μA and the acceleration voltage 8 kV. The electron energy was 12–18 eV (nominal) or 70 eV as indicated in Figs 1–6.

Deuterium-labelled derivatives 4-d_1 and 4-d_2 were prepared by dissolution of **4** in MeOD in a small capillary glass tube and evaporating the solvent by heating before introduction. The ion source was equilibrated with CH_3OD.

Compounds **1**–**5** were prepared by known methods. For **1**, reaction of pregnane-3β-ol-20-one with formamide–formic acid followed by reduction with Li–$EtNH_2$ introduced an amine function at C(20). This was selectively trifluoroacetylated with 1 mol of $(CF_3CO)_2O$. Oxidation (CrO_3–H_2SO_4) and reaction with methylamine followed by $NaBH_4$ reduction led to the methylamino function at C(3). Acetylation and selective saponification of the trifluoroacetamide gave **1**.

For **2**, the CH_2NH_2 group was introduced at C(17) by reacting androstane-3β-ol-17-one with nitromethane in the presence of ethylenediamine[13] followed by reduction with lithium aluminium hydride (LAH). It was methylated (conversion into urethane by ethyl chloroformate followed by reduction with LAH) and selectively trifluoroacetylated with 1 mol of $(CF_3CO)_2O$. The amide at C(3) was introduced as above and the trifluoroacetamide selectively saponified.

For **3**–**5**, 3β-amino-17β-androstanol was prepared by LAH reduction of the oxime of androstane-17β-ol-3-one and converted into the urethane with ethyl chloroformate. Oxidation of the OH group at C(17) (CrO_3–H_2SO_4) and reaction with nitromethane as above[13] followed by LAH reduction led to a diamine; the primary amine group at C(20) was selectively trifluoroacetylated as above. The secondary amine at C(3) was formylated (**3**) or acetylated (**4**) or propylated (**5**). Selective saponification of the trifluoroacetamide gave **3**, **4** and **5**, respectively. The same sequence after preliminary exchange of hydrogens at C(2) and C(4) with D (D_2O, CH_3OD, Na) led to 4-d_4.

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